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Influence of the amount of Na_2O and SiO_2 on the sintering behavior and on the microstructural evolution of a Bayer alumina powder

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Abstract

The target of this work is to investigate the effects of the relative amounts of the main impurities usually encountered in an alumina powder obtained from the Bayer process. On that purpose, the amounts of Na_2O and SiO_2 present in a commercial powder, have been modified by doping. The sintering behavior and the microstructure of the sintered ceramics have been investigated. The ratio Na_2O/SiO_2 strongly influences the shrinkage rates during sintering, the final density and the microstructure. From the commercial powder used (P172SB, Aluminium Pechiney Company, Alcan Group, France), it is shown that an increase in Na_2O content significantly slows down the densification and also the grain growth. The effect of an increase in SiO_2 additions is less obvious even if the dilatometric curves also show decreases in the sintering rates, particularly in the temperature range 1200–1400 °C. Contrary to Na_2O, the addition of SiO_2 leads to abnormal grain growth and provokes an increase in the aspect ratio of the grains.

Keywords: A. Sintering; B. Microstructure; D. Al_2O_3; D. SiO_2; Na_2O

1. Introduction

Numerous studies have shown that the presence of small amounts of impurities strongly influences the microstructure and the properties of alumina. This specific work is based on a reactive alumina powder obtained by the Bayer Process (P172SB, Aluminium Pechiney Company, Alcan Group, France). The Bayer process leads to the presence of numerous residual impurities in the final powders. These impurities may come from the initial bauxite or from the process itself. The chemical analysis of the powder P172SB shows mainly the presence of Na_2O, SiO_2, CaO and MgO (Table 1). Na_2O comes from the NaOH which is used to dissolve the alumina from the bauxite. Few studies have been performed on the influence of this oxide. Some say that Na_2O slightly slows down the grain growth but increases densities [1].

SiO_2 mainly comes from the bauxite but small amounts also come from the milling process. Several articles claim that silica increases the sintering rates due to the formation of an intergranular vitreous phase. This phase also decreases the mechanical properties at high temperature as well as the resistance to corrosion. Moreover, SiO_2 leads to inhomogeneous microstructures [2–10].

CaO also mainly comes from the bauxite. Its fraction can be reduced during the Bayer process but remains usually high (>100 ppm) in low cost products. CaO seems to increase the density after sintering at 1700 °C [11]. However, abnormal grains growth is observed at higher temperatures (>1800 °C) for CaO amounts as low as 30 ppm [5–7]. Some authors support the hypothesis that only the dual presence of CaO and SiO_2 is responsible of the abnormal grains growth [12,13].

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Table 1
Characteristics of powder P172SB

	P172SB
BET (m^2/g)	~9
d_{50} (sedigraph) (μm)	0.36
Na_2O (ppm)	550
SiO_2 (ppm)	770
MgO (ppm)	1010
CaO (ppm)	600
Fe_2O_3 (ppm)	115

MgO is a doping agent introduced on purpose by the powder manufacturer. Indeed, it was shown that additions of MgO improve the sintering rates and homogenize the grain size in the sintered parts [2,14–17].

Mixed additions of SiO_2 and MgO allow a good densification due to the vitreous phase and simultaneously, a good homogeneity of the microstructure [4]. This effect is expected with the powder used in this work. Indeed, the presence of 550 ppm Na_2O, 800 ppm SiO_2 and 600 ppm CaO could lead to the formation of a low amount of a liquid phase during sintering. This is highly favorable to the sinterability [14,18–20]. On the other hand, the high amount of MgO (1000 ppm) should lead to a high microstructural homogeneity.

The ratio SiO_2/Na_2O can easily be adjusted during the Bayer process. The determination of an optimum in composition would be of high interest to improve the properties of the final powder. Therefore, the target of this work is to modify the impurities contents of the powder by additions of low amounts of SiO_2 or Na_2O and to investigate the sintering behavior and the final microstructure. The compositions were selected to be compatible with a standard production by the Bayer process and the total amount of impurities was maintained below 4000 ppm.

2. Experimental procedure

The additions of Na_2O and SiO_2 were performed by the liquid route. This way of processing leads to a better dispersion of the doping agents, especially in the present case where the amounts added were very low. The compounds used were CH_3COO-Na, $3H_2O$ (NormaPur AR, Prolabo, Rhône-Poulenc) for Na_2O and Silica gel (Silica Gel, Degussa) for SiO_2. These compounds were selected because they do not modify the pH of the alumina solution in water. For each nuance investigated, 200 g of alumina powder P172SB were mixed with the doping agents in 400 cm^3 of de-ionized water during 4 h with a magnetic stirrer. After drying at 110 °C, the powders were desagglomerated during 2 h in a ball mill with alumina balls (99.5% purity, 19 mm diameter) and using the ratio: 200 g balls/200 g powder. After sieving through 200 μm, the powders were heat treated during 4 h at 300 °C to removed adsorbed water. Then, powders were stored at 110 °C. The specific surface and the grain size were measured for all specimens and no significant differences with the initial powder were observed (specific area ~9 m^2/g, d_{50} ~0.3 to 0.4 μm).

Cylindrical compacts (l_0 ~10 mm, Φ_0 ~10 mm) of powder were prepared by uniaxial pressing under 100 MPa in a stainless steel die in order to perform dilatometric measurements with a Adamel system. Shrinkage curves (δl) versus temperature (T) were recorded using a heating rate of 5 °C/min from room temperature (RT) up to 1550 °C. These curves were converted into density (d) versus temperature (T) assuming an isotropic shrinkage: $d = d_0[l_0/(l_0 - \delta l)]^3$.

Green densities, d_0, were calculated from the measurement of the weight and from the external dimensions of the samples. Cylindrical compacts of powder were also prepared and heat treated to measure density after sintering. The sintering of these compacts followed the schedule:

- 1320 °C/h from RT up to 1000 °C
- 223 °C/h from 1000 °C up to 1540 °C
- Dwell time of 2 h at 1540 °C
- Natural cooling

Sintered densities, d_s, were measured by Archimede's method: $d_s = m_1/(m_1 - m_2)$, where m_1 is the weight of the dried sintered sample and m_2 is the apparent weight of the sintered sample soaked in water.

Sintered compacts for microstructural study were ground and polished on Struers rotopol 11 down to 1 μm with a diamond paste. They were heated (30 min at 1490 °C) to reveal the grains boundaries and the microstructure and were examined by scanning electron microscopy after gold coating. Microstructures were observed with SEM (Jeol 840, Jeol Ltd., Tokyo, Japan) and the grain size was characterized using Optimas image analysis software. The effective impurity compositions of the alumina samples have been controlled after sintering by I.C.P. spectrometry.

3. Experimental

3.1. Control of the chemical compositions

The comparison between the targeted compositions and effective values controlled after sintering is given in Table 2. It can be noticed that the targeted and measured compositions for SiO_2 doping are in very good agreement (Fig. 1b). On the contrary, the Na_2O doping is less efficient. The controlled values are less than half of the initial target (Fig. 1a).

3.2. Sintering behavior

When looking at the sintering behavior from the dilatometric measurements, it can be noticed that the

Table 2
Chemical compositions of the nuances investigated

Reference	Na_2O target	Na_2O control	Na_2O addition (target)	Na_2O addition control
Standard		550		
N1	650	550	100	0
N2	700	650	150	100
N3	800	650	250	100
N4	1000	750	450	200
N5	1200	850	650	300
N6	1500	1000	950	450
N7	2000	1150	1450	600
N8	2750	1550	2200	1000
N9	3500	1850	2950	1300
N10	7000	3350	6450	2800
	SiO_2 target	SiO_2 control	SiO_2 addition (target)	SiO_2 addition control
Standard		770		
S1	900	920	130	150
S2	1000	1040	230	270
S3	1100	1080	330	310
S4	1200	1160	430	390
S5	1500	1510	730	740
	MgO target	MgO control	MgO addition (target)	MgO addition control
Standard		1010		
M1	1500	1460	490	450
M5	2000	1770	990	760

increase in Na_2O from 550–1150 ppm slows down the densification at low temperature (Fig. 2a). For a given temperature, the derivative curves clearly show a lowering of the densification rates in the range 1050–1280 °C and, conversely, an increase over 1280 °C (Fig. 3a). However, it can be noticed that the value of maximal rate almost remains the same for all the specimens (~0.005 g/cm^3/°C) but shifts down from 1420 to 1380 °C. The opposite situation is observed when Na_2O increases from 1150 to 1850 ppm (Figs. 2b and 3b), the densification rates increase at temperatures lower than 1280 °C and decrease over. The temperature for the maximal densification rate shifts up from 1380 to 1420 °C.

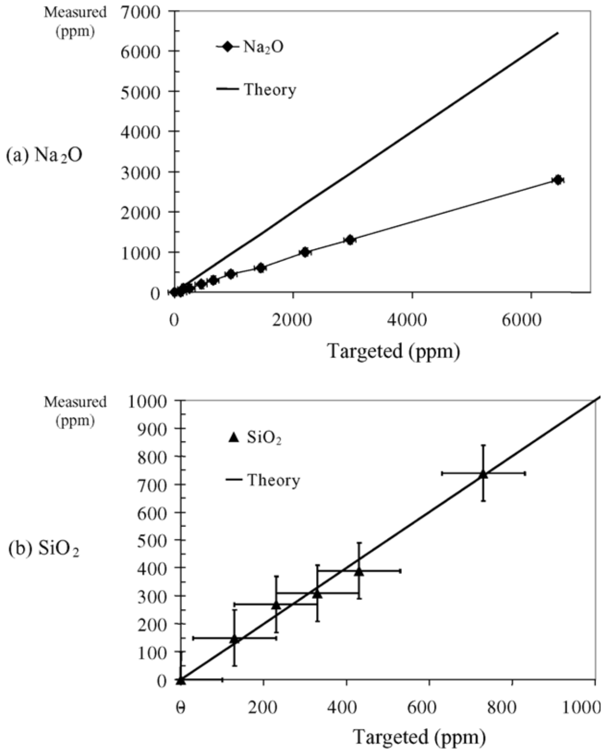


Fig. 1. Comparison of the effective and targeted amounts of doping agent.

An increase in SiO_2 affects in the same way the sintering behavior but the effect of the SiO_2 occurs at higher temperature (over 1150 °C) than with Na_2O (Figs. 2c and 3c). It can be seen that the sintering rates seriously slow down in the range 1150–1450 °C and increase over. On the contrary to Na_2O, the temperature for the maximal rate shifts up to 1500 °C and the value for the maximal rate significantly increases (from 0.005 g/cm^3/°C up to >0.006 g/cm^3/°C).

The densities measured after sintering 2 h at 1540 °C are significantly lower when Na_2O increases (Fig. 4a). On the contrary the variations in density with the amount of SiO_2 are less obvious even if a maximum seems to be observed for specimens with 1040–1080 ppm SiO_2 (Fig. 4b).

3.3. Microstructures

SEM observations have been performed after sintering. The distribution in grain size and the measurement of the average grain size d_{50} has been determined by image analysis of the SEM pictures. In the case of additions of

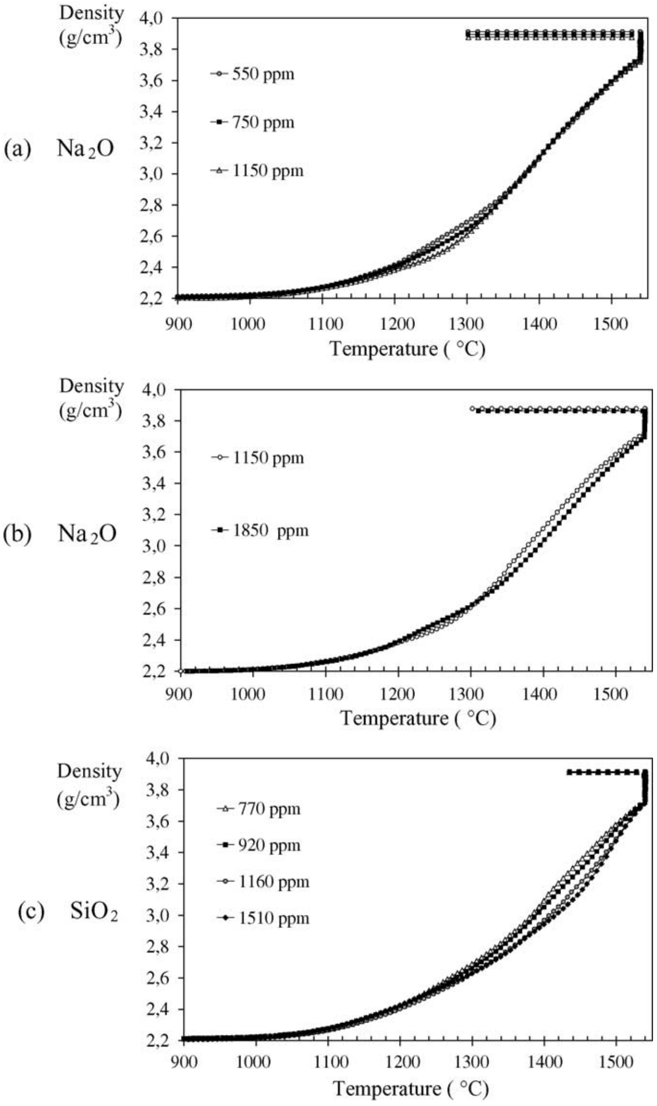


Fig. 2. Influence of Na_2O and SiO_2 on the sintering behaviour.

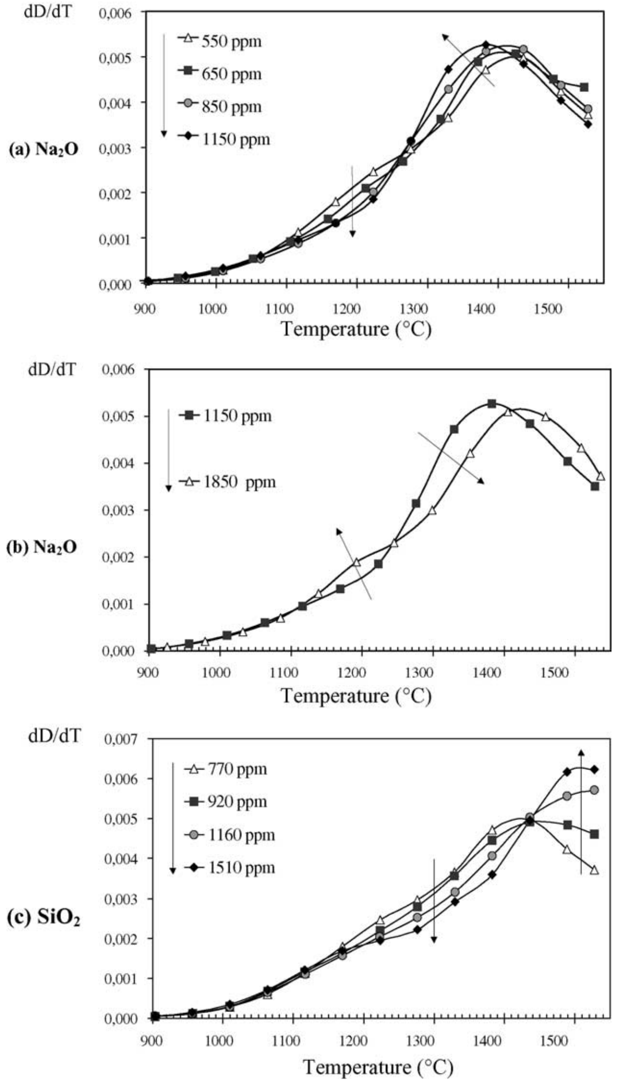


Fig. 3. Influence of Na_2O and SiO_2 on the sintering behaviour (derivative curves).

Na_2O, the cumulative curves (Fig. 5) and the variation of the d_{50} (Fig. 6a) clearly show the decrease in grain size. Simultaneously, the SEM pictures show a better homogeneity of the grain size when the amount of Na_2O increases (Fig. 7).

On the contrary, the increase in SiO_2 does not strongly influence the average grain size (Fig. 6b) but leads to abnormal grain growth (Fig. 7). Moreover, the aspect ratio of the grains also seems to increase with SiO_2.

4. Discussion

4.1. Efficiency of the doping

It has been shown that the amounts of Na_2O controlled after sintering are less than half of the initial target. The sodium acetate used as doping agent decomposes at low temperature to form Na_2CO_3. At higher temperature (> 800 °C), this carbonate melts and decomposes into Na_2O. This phenomenon was also observed by Sumita and Bowen [1]. In the present case Na_2O can form a liquid phase with SiO_2 at temperatures as low as 800 °C. Moreover, Na has a very low vaporization temperature (882.9 °C) and may easily evaporate from this liquid phase. On the contrary, the addition of SiO_2 from the silica gel is very efficient and the measured values after sintering are in fairly good agreement with the amounts initially introduced.

4.2. Sintering and microstructures

Considering the types and amounts of impurities present in the samples (Na_2O, SiO_2, MgO, CaO, etc.), it can be

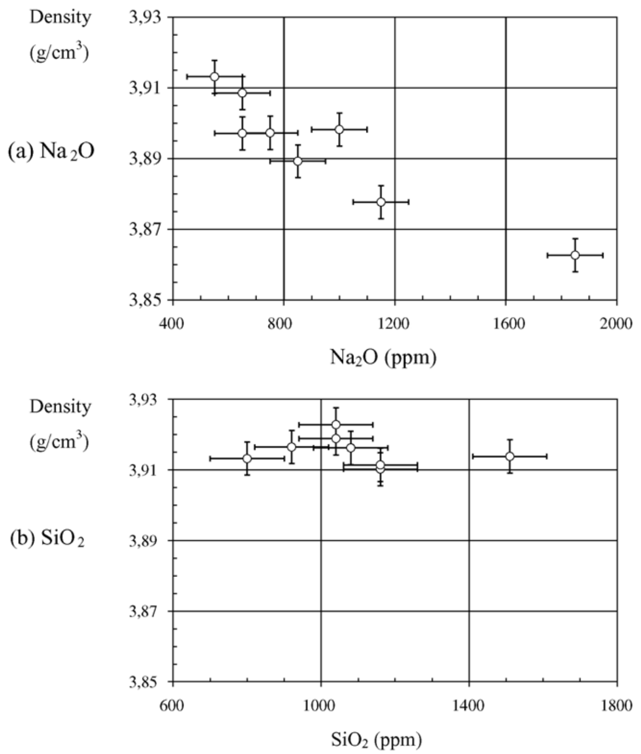


Fig. 4. Variation of the density after sintering 2 h/1540 °C vs. the content of Na_2O or SiO_2.

assumed that the main part of the impurities would concentrate in the grain boundaries and form an intergranular phase. According to the composition of this phase, a more or less large amount of liquid may be present at temperatures lower than the maximal temperature of sintering (1540 °C). If the system Na_2O–CaO–SiO_2 is considered, it can be seen that a partially liquid phase may arise for temperature as low as 1000 °C (Fig. 8). Consequently, the sintering of this alumina powder may take place in the presence of variable amount of liquid phase.

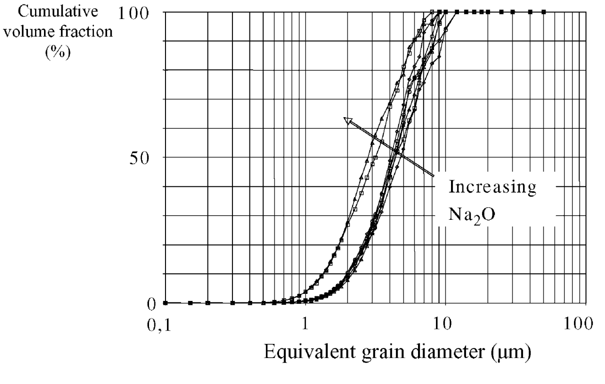


Fig. 5. Grain size distribution from image analysis of the SEM pictures.

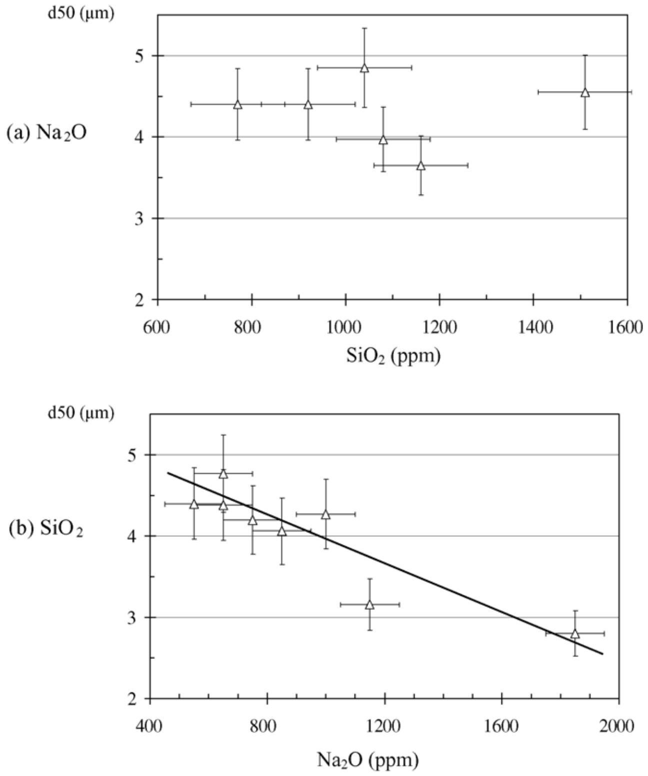


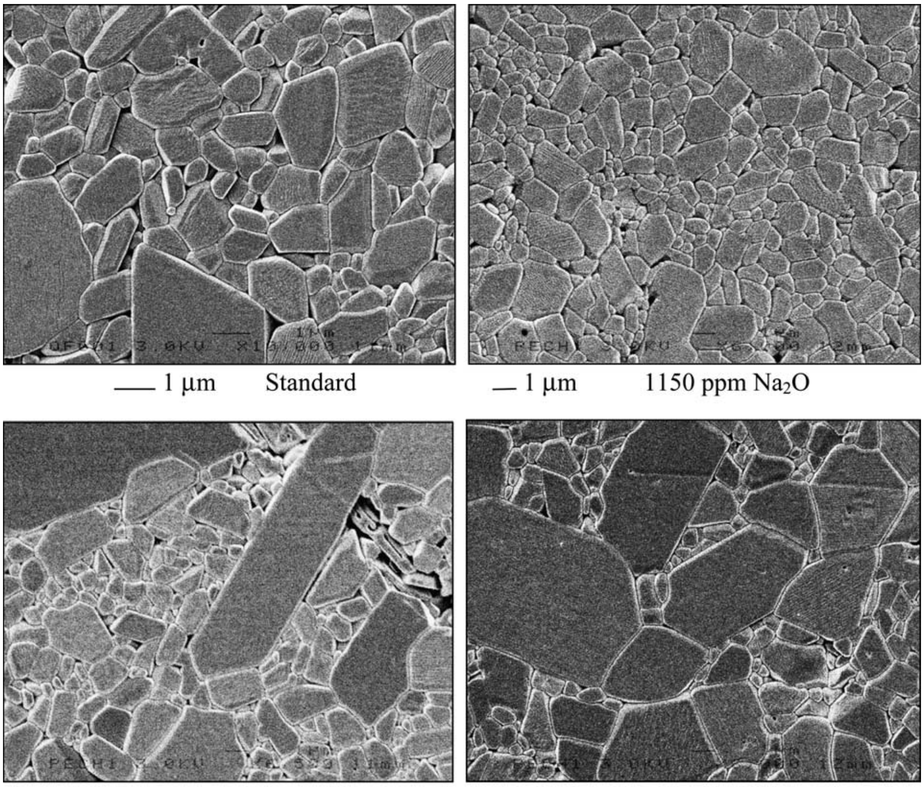
Fig. 6. Average grain size (d_{50}) vs. the content of Na_2O and SiO_2.

Unfortunately, in the present case, the large number of impurities (SiO_2, Na_2O, CaO, MgO, Fe_2O_3, etc.) and the accuracy for the quantitative measurement for each compound do not allow the determination of the exact composition of the sample and consequently its behavior during heating. Only assumption can be proposed to explain the effect of the addition of SiO_2 and Na_2O.

In the case of Na_2O additions, the lower densification rates below 1280 °C are not compensated by higher rates over 1280 °C so that the sintered density is less. On the contrary, with SiO_2 additions, the higher sintering rates at high temperature just lead to little variation in density. It can be supposed that the addition of SiO_2 sufficiently lowers the melting temperature of the intergranular phase so that significant amount of a liquid phase arises in the specimens before reaching the maximal temperature of sintering. This would explain the high densification rates around 1500 °C and also the abnormal grain growth.

In the case of the Na_2O doping, it can be assumed that only a very little amount of liquid is present in the intergranular phase and this amount may even decrease with the addition of Na_2O. This would explain the low final density and the fine microstructure.

Another study, based on a very pure alumina powder doped with a simple system $Na_2O + SiO_2$ will be necessary to understand better the sintering mechanism.



1 µm Standard

1 µm 1150 ppm Na_2O

1 µm 1080 ppm SiO_2

1 µm 1500 ppm SiO_2

Fig. 7. SEM observations after sintering 2 h/1540 °C.

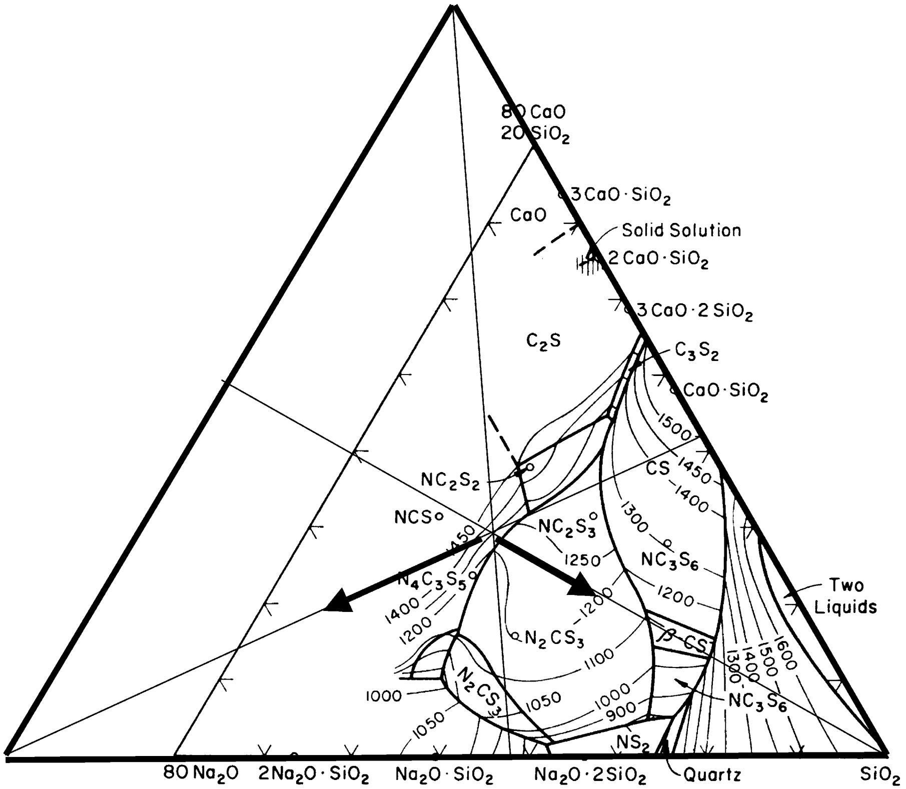


Fig. 8. SiO_2–Na_2O–CaO phase diagram.

5. Conclusion and perspectives

With this work it was shown that the ratio Na_2O/SiO_2 in a Bayer alumina powder strongly influences the behavior during sintering and final microstructure. The Na_2O and SiO_2 form an intergranular phase with all other impurities. The behavior of this phase with the increase in temperature depends on its composition. Unfortunately, in the present case the alumina powder contains a high number of impurities (Na_2O, CaO, SiO_2, MgO, Fe_2O_3, etc.). This situation makes difficult the determination of the exact composition of this phase and even more difficult the study of its behavior with the temperature.

Even so, it was shown that the modification of the standard composition of the commercial Bayer powder investigated by an increase in Na_2O content slows down the densification and leads to lower sintered densities. On the other hand, this increase in Na_2O has a positive effect on the grain size and leads to a fine homogeneous microstructure. On the contrary, the addition of SiO_2 does not affect significantly the final density but leads to abnormal grain growth and increases the aspect ration of the grains.

For a better understanding of the mechanisms involved, a more simple system of impurities should be investigated. Therefore, a future work will focus on the doping of a very pure alumina powder with SiO_2 and Na_2O.

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